

Quasiclassical theory of quantum defect and spectrum of highly excited rubidium atoms

Ali Sanayei and Nils Schopohl*

Institut für Theoretische Physik and

*CQ Center for Collective Quantum Phenomena and their Applications in LISA⁺,
Eberhard-Karls-Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany*

Jens Grimm, Markus Mack, Florian Karlewski, and József Fortágh[†]

Physikalisches Institut and

*CQ Center for Collective Quantum Phenomena and their Applications in LISA⁺,
Eberhard-Karls-Universität Tübingen, Auf der Morgenstelle 14, D-72076 Tübingen, Germany
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We report on a significant discrepancy between recently published highly accurate variational calculations and precise measurements of the spectrum of Rydberg states in ⁸⁷Rb on the energy scale of fine splitting. Introducing a modified effective single-electron potential we determine the spectrum of the outermost bound electron from a standard WKB approach. Overall very good agreement with precise spectroscopic data is obtained.

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I. INTRODUCTION

The spectrum of the outermost bound electron of an alkali atom like ⁸⁷Rb is hydrogen like, but lacks the n^2 -degeneracy of the eigenstates labeled by the principal quantum number n of the pure Coulomb potential [1],[2]

$$E_{n,l} = -\frac{1}{(n - \delta_l)^2}. \quad (1)$$

This effect is the well-known quantum defect δ_l , resulting from the interaction of the outermost electron with the ionic core of the atom and the nucleus. In a refined version of the statistical Thomas-Fermi theory [3], an effective potential determining the interaction between the outermost electron and the nucleus can accurately be modeled by a spherically symmetric potential $V_{\text{eff}}(r; l)$ depending on the distance r from the center and depending on the orbital angular momentum $l \in \{0, 1, 2, \dots, n-1\}$ [4, 5],[2]:

$$V_{\text{eff}}(r; l) = -2 \left[\frac{Z_{\text{eff}}(r; l)}{r} + V_{\text{pol}}(r; l) \right] \quad (2)$$

Here the function $Z_{\text{eff}}(r; l)$ represents a position-dependent weight function that interpolates the value of the charge between unity for large r and charge number Z near to the nucleus for $r \rightarrow 0$, and $V_{\text{pol}}(r; l)$ represents a short-ranged interaction taking into account the static electric polarizability of the ionic core [1, 6].

Overall good agreement with spectroscopic data of alkali atoms (but discarding the fine splitting) has been

reported in [5] choosing

$$Z_{\text{eff}}(r; l) = 1 + (Z-1)e^{-ra_1(l)} - re^{-ra_2(l)} [a_3(l) + ra_4(l)] \quad (3)$$

and

$$V_{\text{pol}}(r; l) = \frac{\alpha_c}{2} \frac{1 - \exp \left[- \left(\frac{r}{r_c(l)} \right)^6 \right]}{r^4}. \quad (4)$$

A table of the parameters $a_1(l)$, $a_2(l)$, $a_3(l)$, $a_4(l)$, α_c , and $r_c(l)$ can be found in [5].

In an attempt to also describe the fine splitting of the excitation spectrum of the outermost electron of ⁸⁷Rb, it has been suggested [4] to superimpose *a posteriori* a spin-orbit term

$$\tilde{V}_{\text{SO}}(r; j, l) = \frac{V_{\text{SO}}(r; j, l)}{[1 - \alpha^2 V_{\text{eff}}(r; l)]^2}, \quad (5)$$

on the potential $V_{\text{eff}}(r; l)$, which then influences the spectrum $E_{n,j,l}$ on the scale of fine splitting and the orbitals $\psi_{n,j,l}(r)$ accessible to the outermost electron. Here

$$V_{\text{SO}}(r; j, l) = \alpha^2 \frac{1}{r} \frac{\partial V_{\text{eff}}(r; l)}{\partial r} g(j, l), \quad (6)$$

and $\alpha = \frac{\lambda_C}{a_B} \simeq \frac{1}{137.036}$ denotes the fine-structure constant, and

$$g(j, l) = \begin{cases} 0 & \text{if } l = 0, \\ \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2} & \text{if } l \geq 1, \end{cases} \quad (7)$$

where $j \in \{l - \frac{1}{2}, l + \frac{1}{2}\}$. To determine those orbitals (with principal quantum number $n = n_r + l + 1$ and radial quantum number $n_r \in \mathbb{N}_0$), a normalizable solution to the Schrödinger eigenvalue problem for the radial

* nils.schopohl@uni-tuebingen.de

[†] fortagh@uni-tuebingen.de

wavefunction $U_{n,j,l}(r) = rR_{n,j,l}(r)$ and associated eigenvalues $E_{n,j,l} < 0$ is required:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \tilde{V}(r; j, l) - E_{n,j,l} \right] U_{n,j,l}(r) = 0, \quad (8)$$

where

$$\tilde{V}(r; j, l) = V_{\text{eff}}(r; l) + \tilde{V}_{\text{SO}}(r; j, l) \quad (9)$$

denotes the effective single-electron potential.

A highly accurate variational calculation of the excitation spectrum of the outermost electron of ^{87}Rb has been carried out recently [7], in which the authors expand the radial wavefunction of the Schrödinger eigenvalue problem (8) in a basis spanned by 500 Slater-type orbitals (STOs). On the other hand, modern high precision spectroscopy of Rydberg levels of ^{87}Rb has been conducted recently. Millimeter-wave spectroscopy employing selective field ionization allows for precise measurements of the energy differences between Rydberg levels [8]. An independent approach is to perform purely optical measurements on absolute Rydberg level energies by observing electromagnetically induced transparency (EIT) [9, 10]. However, there is a systematic discrepancy between variational calculations and the spectroscopic measurements of the fine splitting

$$\Delta E_{n,l} = E_{n,l-\frac{1}{2},l} - E_{n,l+\frac{1}{2},l} \quad (10)$$

as shown in Tables I and II. Given the fact that the error bars of the independent experiments [8, 10] are below 1.1 MHz down to 20 kHz, and on the other hand considering the high accuracy of the numerical calculations presented in [7], such a discrepancy between experiment and theory is indeed significant.

So, what could be the reason for the reported discrepancies? First, it should be pointed out that in the variational calculations [7] a slightly different potential was used, that is,

$$V(r; j, l) = V_{\text{eff}}(r; l) + V_{\text{SO}}(r; j, l). \quad (11)$$

Certainly, within the first-order perturbation theory there exists no noticeable discrepancy in the spectrum of the outermost electron on the fine-splitting scale, when taking into account the spin-orbit forces with $V_{\text{SO}}(r; j, l)$ instead of working with $\tilde{V}_{\text{SO}}(r; j, l)$. This is due to the differences being negligible for $r > Z\alpha^2$. However, since $V_{\text{SO}}(r; j, l)$ eventually dominates even the contribution of the centrifugal barrier term $\frac{l(l+1)}{r^2}$ within the tiny region $0 < r \lesssim \alpha^2 Z$, a subtle problem with a non-normalizable radial wavefunction $U_{n,j,l}(r)$ emerges when attempting to solve the Schrödinger eigenvalue problem for any $l > 0$ with the potential $V_{\text{SO}}(r; j, l)$. Such a problem is absent when one works with $\tilde{V}_{\text{SO}}(r; j, l)$ [4].

A variational calculation with the potential (11) employing $N = 500$ normalizable STOs as basis functions

thus engenders a systematic (small) error of the matrix elements calculated in [7] on the fine-splitting scale. When employing substantially more STOs this error would certainly become larger. With $N = 500$ STOs the discrepancy of these theoretical results with the high precision spectroscopic data, as shown in Tables I and II, is far too large to be corrected by simply replacing $V_{\text{SO}}(r; j, l)$ with $\tilde{V}_{\text{SO}}(r; j, l)$. Hence another explanation is required.

II. QUASICLASSICAL APPROACH AND FINE SPLITTING OF THE HIGHLY EXCITED ^{87}Rb

In 1941 alkali atoms have already been studied in the context of modern quantum mechanics in the seminal work by Goeppert Mayer [3], who emphasized the exceptional role of the $l = 1$ and $l = 2$ orbitals. According to Goeppert Mayer, the outermost electron of an alkali atom is governed by an effective r -dependent charge term

$$Z_{\text{eff}}(r) = 1 + (Z - 1)F(r), \quad (12)$$

where the function $F(r)$ has been determined by employing the semi-classical statistical Thomas-Fermi approach to the many-electron-atom problem, posing the boundary conditions as $\lim_{r \rightarrow 0} F(r) = 1$ and $\lim_{r \rightarrow \infty} F(r) = 0$. As discussed by Schwinger [12], this approach ceases to be valid in the inner shell region $Z^{-1} < r < Z^{-\frac{1}{3}}$ of the atom. Therefore, taking into account the fine splitting in the spectrum of the outermost electron of alkali atoms *a posteriori* by simply adding the phenomenological spin-orbit term (5) to (2), resulting in the effective single-electron potential (9), seems to be questionable on general grounds in that inner shell region.

On a more fundamental level, the treatment of relativistic effects in multi-electron-atom spectra requires an *a priori* microscopic description based on the well-known Breit-Pauli Hamiltonian [13, 14]

$$\mathcal{H} = \mathcal{H}_{\text{nr}} + \mathcal{H}_{\text{rs}} + \mathcal{H}_{\text{fs}}. \quad (13)$$

Here \mathcal{H}_{nr} is the ordinary *nonrelativistic* many-electron Hamiltonian, while the *relativistic corrections* are represented by the perturbation operators \mathcal{H}_{rs} and \mathcal{H}_{fs} . The perturbation term \mathcal{H}_{rs} contains all the relativistic perturbations like *mass correction*, one- and two-body *Darwin terms*, and further the *spin-spin contact* and *orbit-orbit* terms, which all commute with the total angular momentum \mathbf{L} and total spin \mathbf{S} , thus effectuating only small *shifts* of the spectrum of the nonrelativistic Hamiltonian \mathcal{H}_{nr} . The perturbation operator \mathcal{H}_{fs} on the other hand breaks the rotational symmetry. It consists of the standard *nuclear spin-orbit*, the *spin-other-orbit*, and the *spin-spin dipole* interaction terms, which all commute with $\mathbf{J} = \mathbf{L} + \mathbf{S}$, but not with \mathbf{L} or with \mathbf{S} separately, thus inducing the fine splitting of the nonrelativistic spectrum.

Although the proposed functional form of the potential (11) is highly plausible on physical grounds outside the inner core region $r > Z^{-\frac{1}{3}}$, *prima facie* it ap-

TABLE I. Fine splitting $\Delta E_{n,l=1}$ for P states in [MHz].

State $ n, l=1\rangle$	Exp. [11]	Exp. [8]	Theory [7]	Theory (this work)
8P	$565.1(4) \times 10^3$	N/A	602.00×10^3	567.75×10^3
10P	$219.1(4) \times 10^3$	N/A	231.87×10^3	218.77×10^3
30P	N/A	4246.30(5)	4500.50	4246.46
35P	N/A	2566.41(32)	2717.41	2566.28
45P	N/A	1144.09(13)	1217.24	1143.95
55P	N/A	605.77(7)	644.81	605.68
60P	N/A	460.76(5)	480.32	460.68

TABLE II. Fine splitting $\Delta E_{n,l=2}$ for D states in [MHz].

State $ n, l=2\rangle$	Exp. [11]	Exp. [8]	Exp. [10]	Theory [7]	Theory (this work)
8D	$30.4(4) \times 10^3$	N/A	N/A	113.17×10^3	36.42×10^3
10D	$14.9(2) \times 10^3$	N/A	N/A	52.05×10^3	16.56×10^3
30D	N/A	452.42(18)	452.5(11)	1447.53	456.13
35D	N/A	279.65(10)	280.4(11)	894.84	281.52
45D	N/A	128.33(4)	127.8(11)	407.64	128.98
55D	N/A	69.17(2)	69.4(11)	223.71	69.47
57D	N/A	61.98(2)	62.2(11)	197.39	62.24

pears to be inconsistent to lump the aforementioned relativistic many-body forces into an effective single-electron potential of the functional form (11), so that it provides an accurate description also for small distances $Z^{-1} < r < Z^{-\frac{1}{3}}$.

In the absence of a better microscopic theory for an ef-

fective single-electron potential $V_{\text{eff}}(r; j, l)$ describing the fine splitting of the spectrum of the outermost electron in the alkali atoms, we introduce a *cutoff* at a distance $r_{\text{so}}(l)$ with $Z^{-1} < r_{\text{so}}(l) < Z^{-\frac{1}{3}}$ so that the effective single-electron potential is now described by the following modified potential:

$$\tilde{V}_{\text{mod}}(r; j, l) = \begin{cases} V_{\text{eff}}(r; l) & \text{if } 0 \leq r \leq r_{\text{so}}(l), \\ V_{\text{eff}}(r; l) + V_{\text{SO}}(r; j, l) & \text{if } r > r_{\text{so}}(l). \end{cases} \quad (14)$$

The choice [2]

$$r_{\text{so}}(l=1) = 0.029483 \times r_c(l=1) = 0.0442825, \quad (15)$$

$$r_{\text{so}}(l=2) = 0.051262 \times r_c(l=2) = 0.2495720,$$

gives a surprisingly accurate description of the fine splitting in the spectroscopic data for all principal quantum numbers n , see Tables I and II.

The calculation of the spectrum of the outermost bound electron is then reduced to solving the radial Schrödinger equation (8) with the modified potential $\tilde{V}_{\text{mod}}(r; j, l)$. The resulting spectrum is actually hydrogen like, that is,

$$E_{n,j,l} = -\frac{1}{(n - \Delta_{j,l})^2}, \quad (16)$$

where $\Delta_{j,l}$ denotes a quantum defect comprising also the fine splitting. In actual fact the quantum defect describes a reduction of the number of nodes n_r of the radial wavefunction for $l = 0, 1, 2$ as a result of the short-range interaction of the outermost electron with the ionic core

of the atom. Because the higher the orbital angular momentum quantum number l , the lower the probability of the electron being located near to the center, it is clear that the quantum defect decreases rapidly with increasing orbital angular momentum l . Therefore, $\Delta_{j,l}$ is only notably different from zero for $l = 0, 1, 2$.

Writing $\Delta_{j,l} = \delta_l + \eta_{j,l}$ with $\eta_{j,l} \ll \delta_l$, the fine splitting to leading order in α^2 is:

$$\Delta E_{n,l} = 2 \frac{\eta_{l-\frac{1}{2},l} - \eta_{l+\frac{1}{2},l}}{(n - \delta_l)^3} \quad (17)$$

The quasiclassical momentum $p \equiv \sqrt{-Q}$ of the bound electron with orbital angular momentum $l > 0$, total angular momentum $j = l \pm \frac{1}{2}$, and taking into account the Langer shift $l(l+1) \rightarrow (l + \frac{1}{2})^2$ in the centrifugal barrier [15, 16], is then given by

$$Q(r; j, l, E) = \frac{(l + \frac{1}{2})^2}{r^2} + \tilde{V}_{\text{mod}}(r; j, l) - E. \quad (18)$$

For $l = 0$ the centrifugal barrier term and the spin-orbit potential are absent.

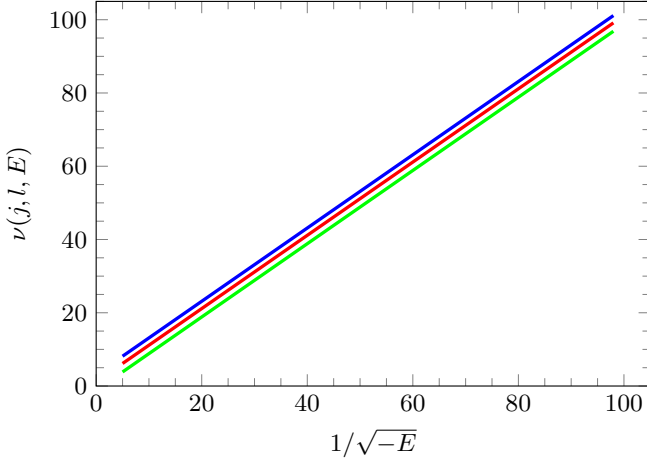


FIG. 1. (Color online) The action integral $\nu(j, l, E)$ associated with the effective single-electron potential $\tilde{V}_{\text{mod}}(r; j, l)$ vs. scaled energy $\frac{1}{\sqrt{-E}}$ for $l = 0$ (blue line), $l = 1$ (red line), $l = 2$ (green line), all for $j = l + \frac{1}{2}$. The curves for $j = l - \frac{1}{2}$ only differ by a tiny shift proportional to α^2 .

Considering high excitation energies $E < 0$ of the bound outermost electron, i.e. a principal quantum number $n \gg 1$, the respective positions of the turning points $r^{(\pm)}$ are given approximately by

$$r^{(-)} = \frac{(l + \frac{1}{2})^2}{1 + \sqrt{1 + (l + \frac{1}{2})^2 E}} \quad \text{if } l \geq 3, \quad (19)$$

$$r^{(+)} \simeq \frac{1}{-E} \left[1 + \sqrt{1 + \left(l + \frac{1}{2}\right)^2 E} \right] \quad \text{if } l \geq 1,$$

where $0 < l \ll \frac{1}{\sqrt{-E}}$. Of course for $l = 0$ only a single (large) turning point $r^{(+)} = \frac{2}{-E}$ exists due to the absence of the centrifugal barrier. However, the lower turning points $r^{(-)}$ are strongly modified for $l = 1, 2$ compared to the pure Coulomb potential case taking into account the core polarization. For $l = 1, 2$ the relation $r^{(-)}(l) \simeq 0.02 \times r_c(l)$ holds; that is, $r^{(-)}(l = 1) \simeq 0.03472$ and $r^{(-)}(l = 2) \simeq 0.12827$ [2]. Since the cutoff $r_{\text{so}}(l)$ in (15) is substantially above those values of the lower turning points $r^{(-)}(l)$, a quasiclassical calculation of the fine-split spectrum of the bound outermost electron is reliable.

For a chosen radial quantum number n_r , the associated eigenvalues $E = E_{n,j,l} < 0$ of the outermost electron now follow from the WKB patching condition [17, 18]:

$$\nu(j, l, E) \stackrel{!}{=} \begin{cases} n_r + 1 & \text{if } l = 0, \\ n_r + \frac{1}{2} & \text{if } l > 0, \end{cases} \quad (20)$$

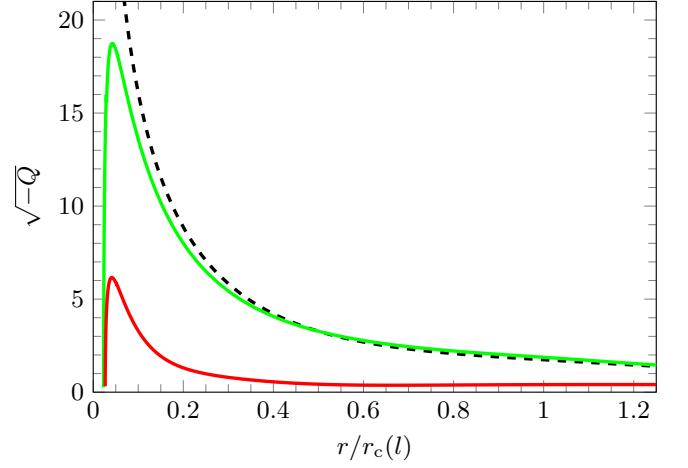


FIG. 2. (Color online) The quasiclassical momentum $\sqrt{-Q}(r; j, l, E)$ vs. scaled distance $\frac{r}{r_c(l)}$ for $l = 0$ (dashed black), $l = 1$ (green), $l = 2$ (red), for $E = E_{n,j,l}$ corresponding to principal quantum number $n = 57$ and $j = l + \frac{1}{2}$. The main contribution to the quantum defect values in (24) originates from the inner core region $r < r_c(l)$.

where $\nu(j, l, E)$ denotes the action integral

$$\begin{aligned} \nu(j, l, E) &= \frac{1}{\pi} \int_{r^{(-)}}^{r^{(+)}} dr \sqrt{-Q}(r; j, l, E) \\ &= \frac{1}{2\pi} \oint dr p(r; j, l, E). \end{aligned} \quad (21)$$

Plotting the function $\nu(j, l, E)$ versus $\frac{1}{\sqrt{-E}}$ for $l = 0, 1, 2$ clearly reveals a linear dependence of the form $\nu(j, l, E) = \frac{1}{\sqrt{-E}} + c(j, l)$, see Fig. 1.

According to [6], for $A, B, C, D \in \mathbb{R}$, with $A > 0$, $B > 0$, $C > 0$, and $|D| \ll C$ the following equality holds:

$$\frac{1}{2\pi} \oint dr \sqrt{-A + \frac{2B}{r} - \frac{C}{r^2} + \frac{D}{r^3}} = \frac{B}{\sqrt{A}} - \sqrt{C} + \frac{BD}{2C\sqrt{C}} \quad (22)$$

For a pure Coulomb potential $A \equiv -E$, $B \equiv 1$, $C \equiv (l + \frac{1}{2})^2$ and $D \equiv \alpha^2 g(j, l)$. The corresponding action integral then reads

$$\nu^{(C)}(j, l, E) = \begin{cases} \frac{1}{\sqrt{-E}} & \text{if } l = 0, \\ \frac{1}{\sqrt{-E}} - (l + \frac{1}{2}) + \frac{\alpha^2 g(j, l)}{2(l + \frac{1}{2})^3} & \text{if } l > 0. \end{cases} \quad (23)$$

It is thus found from WKB theory that the quantum defect associated with the single-electron potential $\tilde{V}_{\text{mod}}(r; j, l)$ is:

$$\Delta_{j,l} = \lim_{E \rightarrow 0^-} [\nu(j, l, E) - \nu^{(C)}(j, l, E)] \quad (24)$$

Ignoring spin-orbit coupling, i.e. for $\alpha = 0$, one has $\Delta_{j,l} \equiv \delta_l$, the standard quantum defect. For $l = 0$ the

TABLE III. The values of quantum defect $\Delta_{j,l}$ associated with the Rydberg level $n = 57$ for $l = 0, 1, 2$.

Quantum defect $\Delta_{j,l}$	Exp. [8]	Exp. [10]	Theory [7]	Theory (this work)
$\Delta_{1/2,0}$	3.1312419(10)	3.13125(2)	3.12791	3.13095
$\Delta_{1/2,1}$	2.6549831(10)	N/A	2.65795	2.65197
$\Delta_{3/2,1}$	2.6417735(10)	N/A	2.64399	2.63876
$\Delta_{1/2,1} - \Delta_{3/2,1}$	0.0132096(14)	N/A	0.01396	0.01321
$\Delta_{3/2,2}$	1.3478971(4)	1.34789(2)	1.35145	1.34851
$\Delta_{5/2,2}$	1.3462733(3)	1.34626(2)	1.34628	1.34688
$\Delta_{3/2,2} - \Delta_{5/2,2}$	0.0016238(5)	0.00163(3)	0.00517	0.00163

centrifugal barrier and the spin-orbit coupling term (6) are zero, so $\Delta_{j,l} \rightarrow \Delta_{\frac{1}{2},0} \equiv \delta_0$.

The dependence of the quasiclassical momentum $\sqrt{-Q(r; j, l, E)}$ on the scaled distance $\frac{r}{r_c(l)}$ is shown for $l = 0, 1, 2$ in Fig. 2. Clearly, it is the inner core region $r^{(-)}(l) < r < r_c(l)$ that provides the main contribution to the quantum defect values. We find, for $l = 0, 2$, that changing the fitting parameter $a_3(l)$ in (3) from its tabulated value in [5] according to the scaling prescription $a_3(l=0) \rightarrow 0.814 \times a_3(l=0)$ and $a_3(l=2) \rightarrow 0.914 \times a_3(l=2)$, leads to a slight downward *constant* shift of the WKB-quantum defect. As a result of this change, the calculated WKB-quantum defect $\Delta_{l \pm \frac{1}{2}, l}$ then agrees well with the spectroscopic data, see Table III. Such a change of $a_3(l)$ does *not* affect the fine splitting values $\Delta E_{n,l}$ though. We also find that the dependence of the fine splitting $\Delta E_{n,l}$ on the principal quantum number n is well described by (17) for all $n \geq 8$, see Tables I and II.

In actual fact, for $r^{(+)} \gg r^{(-)}$, which is a criterion that is always met for high excitation energies $\sqrt{-E} \simeq 0$ of the outermost electron, the uniform Langer-WKB wavefunction $U_{n,j,l}^{(\text{WKB})}(r)$ [19, 20], with $r^{(+)}$ considered as the only turning point, describes the numerical solution $U_{n,j,l}(r)$ to the radial differential equation (8) under the influence of the effective modified single-electron potential (14) rather accurately [21]. Only very near to the second turning point $r^{(-)}$, at a distance smaller than $r_{\text{so}}(l)$, the Langer-WKB wavefunction $U_{n,j,l}^{(\text{WKB})}(r)$ ceases to be a good approximation to the numerical solution $U_{n,j,l}(r)$

of the radial Schrödinger equation (8) [21].

III. CONCLUSIONS

In this work we reported a significant discrepancy between experiment [8, 10] and highly accurate variational calculations [7] of the spectrum of Rydberg states of ^{87}Rb on the energy scale of the fine splitting. We discussed that the usual *a posteriori* adding of the relativistic spin-orbit potential to the effective single electron potential governing the outermost electron of alkali atoms is indeed inconsistent inside the inner atomic core region. In the absence of a full microscopic theory that lumps all many-body interactions together with the relativistic corrections into an effective single-electron potential in a consistent manner, we suggested a modified effective single-electron potential, see (14), that enables a correct description of the spectrum of Rydberg states on the fine splitting scale in terms of a simple WKB-action integral for all principal quantum numbers $n \geq 8$. Modern precision spectroscopy of highly excited Rydberg states thus enables the probing of the multi-electron correlation problem of the ionic core of alkali atoms. This is certainly a fascinating perspective for further experiments and theoretical studies.

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